Ruthenium (II) Complexes Immobilized on Swellable Polyacrylate Matrices: Synthesis and Catalytic Applications

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ABSTRACT: $RuH_2(PPh_3)_4$ has been immobilized on swellable polyacrylate matrices to provide heterogenized carboxylate-derivatives. These swellable polymer supported ruthenium (II) complex catalysts have been used in the transfer hydrogenation of aldehydes. Hydrogen donors are formate salt, cyclohexanol, and benzyl alcohol. The catalysts exhibit good activity for hydrogen transfer reduction of aldehydes. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3262–3269, 2008

Key words: ruthenium; swellable polyacrylate matrices; hydrogen transfer hydrogenation; aldehyde; hydrogen donor

INTRODUCTION

The preparation and application of polymer supported catalysts has attracted widespread attention over the past few decades. Serious interest in these catalysts originated with efforts to develop catalytic systems displaying the high activity, selectivity, and reproducibility typical of homogeneous catalysts, combined with easy separability and recovery characteristic of heterogeneous catalysts.[1–3] Recently, Nomura and Kuromatsu[4] reported the preparation of various pyridine and 2,2′-bipyridyl ligands attached to the polymer chain end of ring-opened poly(norbornene) by living ring-opening metathesis polymerization (ROMP) using $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}^iPr_2C_6H_3)(O^tBu)_2$. The prepared pyridine and 2,2′-bipyridyl derivatives were used as ligands for catalytic hydrogen transfer reduction of cyclohexanone in the presence of $Ru(acac)_3$ (in toluene/^iPrOH in the presence of NaO^iPr, at 50°C, acac : acetylacetonato). The catalytic activity increased upon addition of the above polymer as the ligand, and the prepared catalyst could be recovered by filtration as the precipitate, by pouring the reaction mixture into methanol. The recovered catalyst could be reused without decrease in the activity.

Several important results have been obtained and the use of polymer supported catalysts has indicated new areas of catalysis. Pittman et al.[5] recently discussed the polymer-supported catalysts and reagents containing frequently employed palladium species used in synthesis. These supported species are less moisture sensitive, less air sensitive, and more easily separated from reaction mixtures. Indeed, in spite of initial enthusiasm, these goals have been, in general, only partially attained. The main drawbacks generally encountered for polymer supported catalysts are related to difficulties in achieving high metal loadings, due to the limited availability of the reactive functionalities, limited catalytic activity, due to diffusion problems, and in the characterization of the anchored metal species. In addition, a critical problem for the long-term use of supported catalysts is loss or leaching of metal from the support.

The porosity and swellability of the polymer supports, and bulkiness of the metal precursor play key roles. To achieve a high specific activity, a significant specific surface area of contact between the substrate and the adsorbed catalytic centers is necessary. This may be achieved either by fine dispersion or by creating a highly developed pore system in the granules of the supports. In the first variation, for example, when very fine beads of lightly crosslinked polystyrene[6] are used, the activity is very much greater than when larger beads or more highly crosslinked materials[7–9] are used. But it is frequently difficult to separate the highly dispersed catalyst particles suspended in the reaction medium from the final products and to reuse it. In the second variation, the increase in the internal surface area by the creation of a high porosity is limited by a decrease in granule strength, since good mechanical properties are required for the catalyst support. A
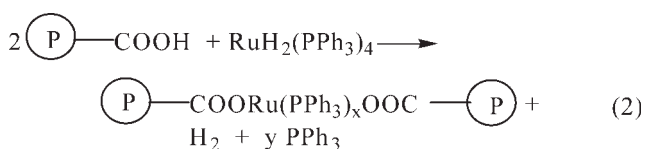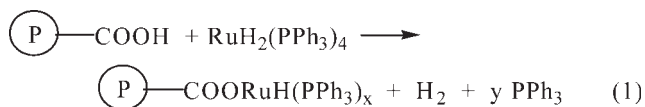

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new type of catalyst system, gel-entrapped or gel-immobilized catalyst systems was proposed by Hines et al.[10] and Kabanov and Smetanyuk.[11] Ideally, polymer swelling by an appropriate liquid phase offers accessibility of active catalytic sites to organic substrates. A high degree of swelling is important for good catalytic activity. In industrial developments, gel-immobilized catalysts systems can offer several advantages from chemical engineering viewpoints.[11] In recent years, superabsorbent polymers have be widely used in many areas, for example, feminine hygiene products, ion-exchange resins, soft contact lenses, and carriers for controlled release of drugs. Because of good swellability in some media, superabsorbent polymers used as a support for catalysts may offer advantages over nonswellable polymer supports, particular if they have the potential to achieve higher metal loadings and higher activities. Synthetic polyacrylates derived from polyacrylic acid have emerged as one important absorbent, since they are fairly inexpensive and easy to polymerize to products of high molecular weight. Because of the existence of functional carboxylic groups they are particularly convenient in providing both bidentate and monodentate ligands for complexation to transition metals.

Polymers with side chain carboxylic groups have been used to prepare catalytic systems which display higher activity and selectivity for the isomerization and hydrogenation of alkenes.[12,13] Soluble carboxylato-(triphenyl-phosphine)ruthenium (II) complexes have been reported by Valentini et al.[14] to be among the more active ruthenium catalysts for the hydrogen transfer from alcohols to aldehydes. The immobilization of ruthenium complexes onto polymer supports containing carboxylate pendants were therefore of interest for the preparation of active and easily reusable ruthenium catalysts. We have reported the preparations of superabsorbent polymers (polyacrylates) by crosslinking acrylic acid and acrylamide copolymer.[15] Applications of this polymer as a swellable support for ruthenium (II) complexes were investigated in this work. The ruthenium precursor chosen for the anchoring reaction was $RuH_2(PPh_3)_4$ which can react with the carboxylic groups of the polymer matrices giving either mono(carboxylato)- or bis(carboxylato)-species [eqs. (1) and (2)].

$$\text{P}—COOH + RuH_2(PPh_3)_4 \longrightarrow$$
$$\text{P}—COORuH(PPh_3)_x + H_2 + y\ PPh_3 \quad (1)$$

$$2\ \text{P}—COOH + RuH_2(PPh_3)_4 \longrightarrow$$
$$\text{P}—COORu(PPh_3)_xOOC—\text{P} + \quad (2)$$
$$H_2 + y\ PPh_3$$

where $x + y = 4$.

Ruthenium (II) complexes supported on swellable polyacrylates were characterized by FTIR. Their catalytic activities are evaluated for transfer hydrogenation reactions. Several recent research works about transfer hydrogenation reactions have been reported. Ogo reported the transfer hydrogenation of ketones with HCO_2Na as a hydrogen donor, catalyzed by achiral Ru (II) complexes.[16] Canivet et al.[17] studied transfer hydrogenation of aromatic ketones to give the corresponding chiral secondary alcohol with sodium formate with arene ruthenium complexes. In this article, we report a series of transfer hydrogenations of aromatic and aliphatic aldehydes catalyzed by superabsorbent supported ruthenium complexes. Hydrogen donors are from formate salt to cyclohexanol and benzyl alcohol. The reaction medium can be either biphasic or an organic phase.

EXPERIMENTAL

Materials

The reagents, hydrated ruthenium trichloride (Engelhard, USA, 39.91 Ru%) and sodium borohydride (B.D.H., Canada, Analytical reagent) were used as received. Triphenylphosphine (Aldrich, USA, 99%) was recrystallized from ethanol before use. The solvents, dimethylformamide (DMF) (J.T. Baker, USA, Baker analyzed reagent), benzene (B.D.H., Canada, analytical reagent), isopropyl alcohol (B.D.H., Canada, analytical reagent), and ethanol (Commercial Alcohols Ltd., Canada, absolute) were used as received. Ruthenium atomic absorption standard solution (Aldrich, USA, 990 ppm) was used as received.

Elemental analysis

Chemical analysis was performed by Guelph Chemical Laboratories Ltd, Guelph, Ontario, Canada.

IR spectra analysis

The infrared spectra of $RuH_2(PPh_3)_4$, naked superabsorbent and superabsorbent supported Ru(II) complexes were obtained using a Nicolet 520 FTIR Spectrophotometer equipped with an IBM PC and Omnic software for spectra subtraction and area calculations. $RuH_2(PPh_3)_4$ spectrum was obtained using nujol mull. Spectra of naked superabsorbent and ruthenium complexes supported on superabsorbent polymer were obtained in KBr disks.

Ruthenium analysis

Direct current plasma (DCP) is well recognized as an accurate, rapid, and very sensitive method and is

widely used for analysis of metals. In this laboratory, the DCP method has previously been used for the analysis of copper, nickel, silver, cobalt, and arsenic metals.[18–20] On the other hand, very little information is available on the DCP analysis of organometallic polymers containing ruthenium. We have examined the DCP technique for the analysis of superabsorbent supported ruthenium complexes. The DCP emission spectrometer used was a SpectraSpan 7 Plasma Emission Spectrometer (SS-7) by ARL Fisons.

The superabsorbent supported ruthenium (II) complex samples for analysis were prepared using the following procedures: 10–15 mg of sample weighed to five decimal places was put in a tall, spoutless beaker covered by a watch glass. Ten milliliter of 1 : 3 volume ratio of concentrated HCl to concentrated HNO_3 acid, respectively, was added. This mixture was heated on a hot plate and refluxed for 24 h. The solution was diluted to 50 mL in a volumetric flask and run on the DCP. The small molecules of $RuH_2(PPh_3)_4$ and $RuCl_2(PPh_3)_3$ were analyzed as references. They were prepared under the same conditions used for the supported ruthenium complex samples. The results show that analyzed composition by weight for $RuH_2(PPh_3)_4$ was 8.78 Ru%. The calculated composition by weight is 8.74 Ru%. The analyzed composition by weight for $RuCl_2(PPh_3)_3$ was 10.06 Ru%; calculated composition is 10.55 Ru%. It is felt that the DCP technique for the analysis of ruthenium metal whether it is supported on polymer support or not is a reliable and precise method.

Synthesis of superabsorbent polyacrylate

Synthesis of superabsorbent polyacrylate with different acrylamide (AM) content in copolymer, referred to as CCPAA absorbents (1.5% AM, 3% AM and 5% AM, less than 250 μm) were prepared from our lab using solution polymerization in the presence of redox initiator. The details for synthesis of superabsorbent polyacrylate are described in our previous paper.[15] The absorption capacities of CCPAA (1.5% AM,) CCPAA (3% AM), and CCPAA (5% AM) for distilled water are 900 g water/g dry polymer, 320 g water/g dry polymer, and 60 g water/g dry polymer, respectively.

Preparation of dihydridotetrakis (triphenylphosphine)ruthenium

$RuH_2(PPh_3)_4$ was prepared according to the procedure described by Levinson and Robinson.[21] In a typical procedure, hydrated ruthenium trichloride (0.795 g, 3.1 mmol) in hot ethanol (40 mL) was added rapidly to a vigorously stirred solution of triphenylphosphine (4.71 g, 18 mmol) in boiling ethanol (200 mL) under a nitrogen atmosphere. Sub-
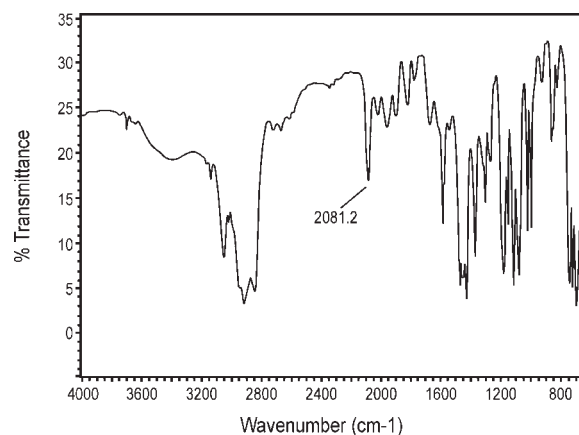

Figure 1 IR Spectrum of $RuH_2(PPh_3)_4$.

sequent, rapid, portionwise addition of sodium borohydride (0.57 g 15 mmol) in hot ethanol (40 mL) gave a yellow precipitate which was filtered off, washed with ethanol, water, and ethanol, and dried in vacuum to give the mustard yellow colored product, $RuH_2(PPh_3)_4$. The IR spectrum includes a single sharp medium metal-hydride stretch at 2081 cm^{-1} (υ_{RuH}) as shown in Figure 1 (lit. 2080 cm^{-1} (Ito et al.).[22] Analyzed composition by weight for $RuH_2(PPh_3)_4$ was C, 74.72%, H, 5.20%, Cl, 0.0%, Ru, 8.78%. Calculated composition by weight for $RuH_2(PPh_3)_4$ is C, 75.05%, H, 5.45%, Cl, 0.0%, Ru, 8.74%.

Preparation of the polycarboxylate ruthenium complexes

Braca et al.[23] reported the preparations of linear polyacrylic acid (PAA) ruthenium complexes using isopropyl alcohol as reaction medium. Valentini et al.[14] supported ruthenium complexes on Amberlite IRC50 resin (800 Å pores size) using tetrahydrofuran (THF) as reaction medium. The use of a microporous resin Kastel C101 (average pores size 30 Å) was completely unsuccessful for the preparation of supported catalysts. In this case the limiting factor seems to be the accessibility of the metal precursor to the carboxylate functions of the resin. We also tried to prepare CCPAA absorbent supported ruthenium complexes using isopropyl alcohol or tetrahydrofuran as reaction medium, but our attempts were also unsuccessful. It seems that these reaction media do not provide sufficient swelling of the support. It is clear from these findings that the swelling of the polymer supports by the reaction medium is also important for achieving higher metal loadings. Therefore, dimethylformamide (DMF) was then chosen as a potentially suitable reaction medium, since it provides a higher swelling of the CCPAA absorbent.

TABLE I
Elemental Analytical Data for CCPAA
Polymeric Support

Sample CCPAA	Elemental analysis			
	C%	H%	O%	N%
1.5% AM	41.44	6.19	31.10	0.55
3% AM	44.02	5.50	36.38	0.64
5% AM	44.81	5.80	39.74	1.04

Elemental analysis data for the CCPAA absorbents (1.5% AM, 3% AM, and 5% AM) are reported in Table I. On the basis of analytical data for C, H, O, and N, the contents of —COO mmol/g absorbent of CCPAA (1.5% AM, 3% AM, and 5% AM) were calculated as 9.52 mmol/g, 11.0 mmol/g, and 12.1 mmol/g, respectively.

A typical procedure for the preparation of CCPAA absorbent supported ruthenium complexes is as follows. 0.30 g dried CCPAA polymer particle size (<250 μm) was allowed to swell for 30 min in refluxing DMF (60 mL) under nitrogen. Appropriate amounts of $RuH_2(PPh_3)_4$ were added dropwise to achieve —COO/Ru molar ratios of 20, 10, or 5 in hot DMF (60 mL) and the solution was refluxed for 40 h. Pale-yellow powders were obtained, which were washed with isopropyl alcohol and benzene to dissolve the unreacted starting materials. The products are referred to as CCPAARu.

X-ray analysis

XRD analysis for $RuH_2(PPh_3)_4$ and CCPAARu were performed using a Philips 1830 diffractometer operated at 40 kV, 30 mA with graphite-filtered CuK_α (λ = 0.154 nm) radiation and a θ compensating slit. Data were acquired in 2θ = 0.05°, 8 s/step. The scanning range is from 3° to 30°. XRD was performed at room temperature.

Catalytic reactions

Transfer hydrogenation of aldehydes was carried out in a nitrogen-flashed 50-mL flask equipped with a reflux condenser, two neoprene-capped side arms and a magnetic bar was immersed in an oil bath thermostated at the designated temperature. The course of the reaction was followed by a Perkin–Elmer AutoSystem Gas Chromatograph coupled with a 1020 PC Plus, using a FID detector. The separations were accomplished with a 30 m × 0.322 cm column which was packed with DB-1 (100% polymethyl siloxane, 0.3 μm film).

RESULTS AND DISCUSSION

Analysis results

Elemental phosphorus analytical data and ruthenium analysis data by the DCP technique are reported in Table II. The ruthenium content of the CCPAA absorbent (1.5% AM) indicates that the amount of supported Ru complexes increased upon decreasing the initial —COO/Ru molar ratio used in the preparation at a reaction time of 40 h. The CCPAA absorbent with a higher crosslinking degree (3% AM) showed much lower ruthenium content, compared to CCPAA absorbent (1.5% AM) at the same reaction condition; this is probably due to lower swellability of the absorbent with higher crosslinking degree.[15,24,25] It was found however that the ruthenium content of the CCPAA (3% AM) supported ruthenium complexes can be increased by increasing the reaction time to 70 h. The swelling is limited for the CCPAA absorbent with higher crosslinking degree (5% AM), the ruthenium content being 0.20% at a reaction time of 70 h. Even by increasing the reaction time to 85 h, the ruthenium content did not increase. The phenomena may be explained on the basis that an increase in the degree of crosslinking lowers the swelling ability of the matrix, thus reducing its ability to undergo functionalization and coordination of the metal.[15,24–26]

FTIR characterization

Taking into account the alternative modes of coordination of carboxylate ligands to a metal, monodentate or bidentate, the following Ru (II) species (Fig. 2) may be present in the heterogenized systems.

TABLE II
Analytical Data of Polymer Supported Metal Complexes

Sample CCPAA	Reaction time (h)	Metal precursor	Ru%	P%	P/Ru	COO/Ru initial
1.5% AM	40	$RuH_2(PPH_3)_4$	4.93	4.95	3.27	5
1.5% AM	40	$RuH_2(PPH_3)_4$	2.91	2.41	2.70	10
1.5% AM	40	$RuH_2(PPH_3)_4$	1.86	1.08	1.90	20
3% AM	40	$RuH_2(PPH_3)_4$	0.32	0.22	2.22	5
3% AM	70	$RuH_2(PPH_3)_4$	2.65	2.37	2.96	5
5% AM	70	$RuH_2(PPH_3)_4$	0.20	0.85	1.35	5
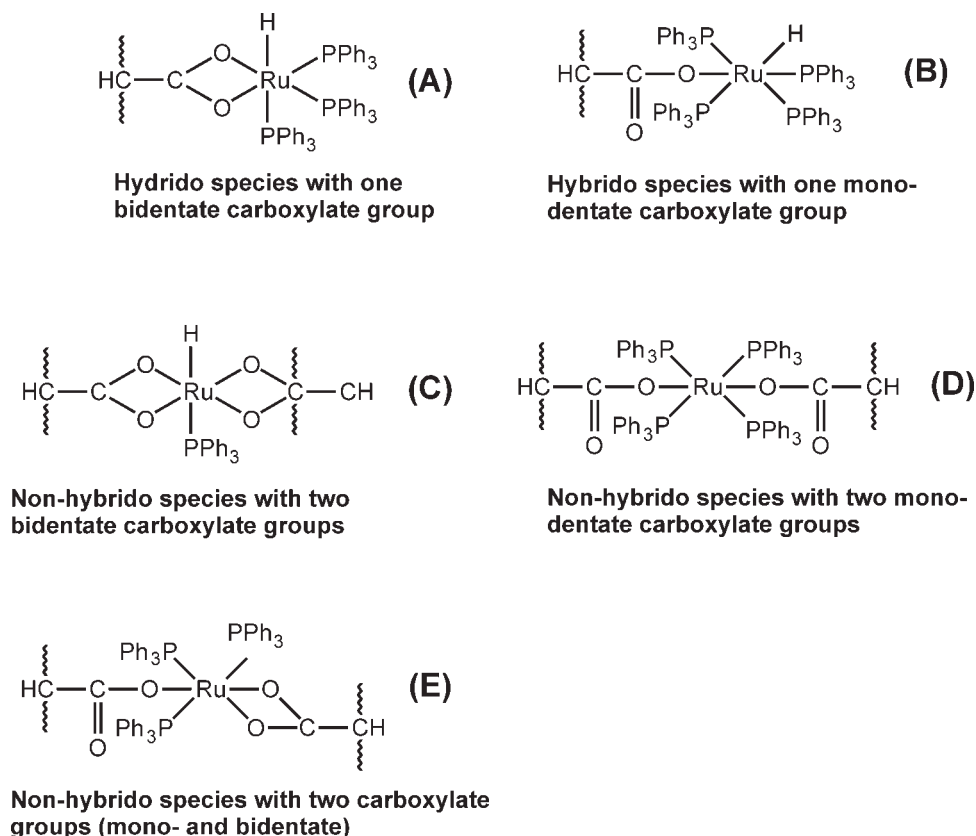
**Figure 2** Possible supported ruthenium species.

The major information on the nature of the coordinated metal species was given by IR spectroscopy. In the IR spectrum of CCPAARu with 4.93 Ru% shown in Figure 3, the band at 1954 cm^{-1}, due to υ(Ru—H) is presented, which indicates that hydrido monocarboxylate species (A and B) are present.

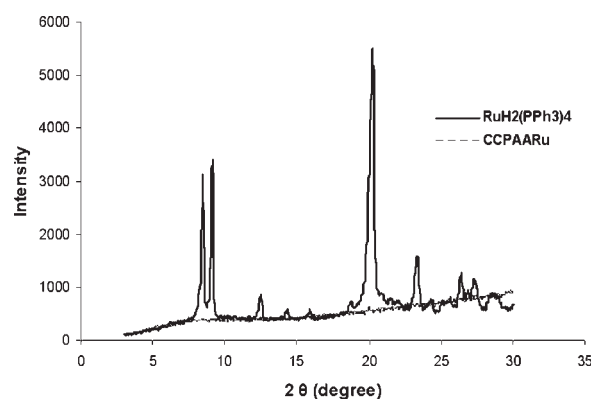The IR absorptions of the carboxylate ligands coordinated to the metal were very weak and partially blurred by strong absorptions of the support [Fig. 3(a,b)]. A computer-aided subtraction of the spectrum of the naked support revealed the presence of absorptions due to the υ_{as} (OCO) and υ_s (OCO) modes together with the bands of PPh$_3$ at 1492 cm^{-1} [Fig. 3(c)].

The absorptions at 1632 and 1399 cm^{-1} and those at 1565 and 1436 cm^{-1} suggest the presence of both one carboxylate (species (A) and (B) in Fig. 2) and two carboxylate ligands (species (C), (D), and (E) in Fig. 2) coordinated to the metal centers.[27,28] Moreover, a comparison between the intensities of the band at 1632 and 1565 cm^{-1} indicates a predominance of the mono-dentate mode of coordination of the carboxylate ligands. In consideration of the high intensity of the band assignable to υ(RuH) and of the high activity of the CCPAARu catalysts in the transfer hydrogenation of aldehydes discussed in the later sections, it suggests that spectrum of CCPAARu in Figure 3(c) indicates the one mono-dentate (species (A)) and one bidentate (species (B)) predominated the metal centers.

In the IR spectra of CCPAARu with 2.91 Ru% and 1.86 Ru%, the band at 1954 cm^{-1}, due to υ(Ru—H) is present also, which indicates that the hydrido monocarboxylate species ((A) and (B)) are present. The absorptions at 1632 and 1399 cm^{-1} and those at 1565 and 1436 cm^{-1} are also present. A comparison
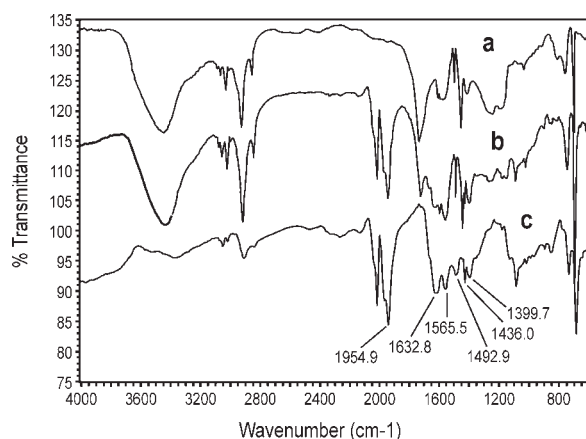
Figure 3 IR Spectrum of CCPAARu (Ru% 4.93). (a) CCPAA, (b) CCPAARu, (c) Computer-aided difference between spectra (b) and (a).

Figure 4 XRD patterns of RuH$_2$(PPh$_3$)$_4$ and CCPAARu.

between the intensities of the band at 1632 cm^{-1} and 1565 cm^{-1} indicates a predominance of the monodentate mode of coordination of the carboxylate ligands. On comparison with the CCPAARu with 4.93 Ru%, the intensity of the band at 1565 cm^{-1} is slightly increased.

XRD characterization

Figure 4 shows the X-ray patterns of RuH$_2$(PPh$_3$)$_4$ and CCPAARu. The diffractogram of RuH$_2$(PPh$_3$)$_4$ demonstrates that it has crystal structure. Since reflections are observed at angles of 8°, 9°, and 20°. When RuH$_2$(PPh$_3$)$_4$ was supported onto the polymer support, the crystal structure did not existed anymore, therefore no reflections are observed for the CCPAARu. On the basis of the elemental analysis and XRD findings, it is confirmed that RuH$_2$(PPh$_3$)$_4$ was supported on the CCPAA polymers.
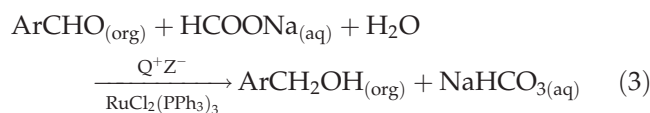
Catalytic applications

Ruthenium (II) complexes supported on superabsorbent polymers were employed for transfer hydrogenation of aldehydes.

The triphasic transfer hydrogenation of aromatic aldehyde by aqueous sodium formate

Bar et al.[29,30] reported the transfer reduction of aromatic aldehydes with HCO$_2$Na as a hydrogen donor,

catalyzed by RuCl$_2$(PPh$_3$)$_3$. Catalytic amounts of quaternary ammonium salts are used under phase transfer conditions [eq. (3)]. It is well known that the activity of the polymer supported catalysts depends on polymer-solvent interactions.[6,13,31] Use of polymer supports containing some units which may have a better affinity for the liquid phase might render the activity sites to be more readily available to the substrate and reduce, or eliminate diffusion control. Until now polymer supported ruthenium (II) complexes have not been used for the transfer hydrogenation of aromatic aldehydes by aqueous sodium formate. We describe this reaction in the presence of CCPAARu, which contains 4.93 Ru%, and a quaternary ammonium salt in eq. (4).

$$ArCHO_{(org)} + HCOONa_{(aq)} + H_2O$$
$$\xrightarrow[RuCl_2(PPh_3)_3]{Q^+Z^-} ArCH_2OH_{(org)} + NaHCO_{3(aq)} \quad (3)$$

Q^+Z^- = Quaternary ammonium salt, Aliquat$^®$ 336 (phase transfer catalyst).

$$ArCHO_{(org)} + HCOONa_{(aq)} + H_2O$$
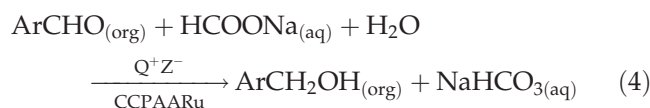$$\xrightarrow[CCPAARu]{Q^+Z^-} ArCH_2OH_{(org)} + NaHCO_{3(aq)} \quad (4)$$

Table III shows the transfer hydrogenation of 2,6-dichlorobenzaldehyde by sodium formate in the presence of CCPAARu (4.93 Ru%) catalysts at different formate concentrations. It can be seen that CCPAARu catalyst exhibited good catalytic activity. The selectivity, metal leaching, recycling of catalyst, and a kinetic study of the systems are reported in our recent article.[32]

Transfer hydrogenation of aromatic aldehyde by cyclohexanol

In the catalytic transfer hydrogenation of aldehydes and ketones to alcohols, using primary and secondary alcohols as hydrogen donors, transition metal salts,[33] CoH$_3$(PPh$_3$)$_3$,[34] RhCl$_2$(PPh$_3$)$_3$,[35] RuCl$_2$ (PPh$_3$)$_3$,[36] IrCl$_3$ [P(OMe)$_3$]$_3$,[37] and RuH$_2$(PPh$_3$)$_4$[38] have been reported

TABLE III
Transfer Hydrogenation of 2,6-Dichlorobenaldehyde by Sodium Formate in the Presence of CCPAARu (4.93 Ru%) Catalysts ($T = 80°$C)

Ru × 10^2 (mmol)	Reaction medium	PTC (mM)	Aldehyde (M)	HCOONa 2 mL	Initial reaction rates (mM/min)	Conversion 4 h
1.22	Chloro-benzene	32.20	0.12	1 M	0.83	88.5
1.22	Chloro-benzene	32.20	0.12	3 M	1.16	91.0
1.22	Chloro-benzene	32.20	0.12	4 M	1.70	96.5
1.22	Chloro-benzene	32.20	0.12	5 M	2.03	100
1.22	Chloro-benzene	32.20	0.12	6 M	1.21	94.1
1.22	Chloro-benzene	32.20	0.12	8 M	0.83	87.1

TABLE IV
Transfer Hydrogenation of 2,6-Dichlorobenzaldehyde from Cyclohexanol in the Presence
of CCPAARu (1.86 Ru%) Catalysts (T = 140°C)

Ru × 10^3 (mmol)	Reaction medium	Alcohol (M)	Aldehyde (M)	Initial reaction rates (mM/min)	Conversion 24 h
6.44	2,6-dichlo-robenzene	0.13	0.13	0.04	32.7
6.44	2,6-dichlo-robenzene	0.26	0.13	0.10	46.1
6.44	2,6-dichlo-robenzene	0.39	0.13	0.18	81.6
6.44	2,6-dichlo-robenzene	0.52	0.13	0.27	90.0

to have catalytic activities as homogeneous transition metal catalysts.

Valentini et al.[14] also reported that heterogenized ruthenium (II) complexes bound to polycarboxylate matrices can be used as a catalyst for the hydrogen transfer from cyclohexanol to hexanal. CCPAARu catalyst which contains 1.86% of ruthenium (II) is used to catalyze hydrogen transfer from cyclohexanol to aromatic aldehydes [eq. (5)]. Furthermore, hydrogenation of aromatic aldehydes is of considerable interest, since aromatic aldehydes are generally cheaper than the corresponding alcohols.

$$Ar—CHO + \text{(cyclohexanol)}—OH \xrightarrow{CCPAARu} Ar—CH_2OH + \text{(cyclohexanone)}=O \quad (5)$$
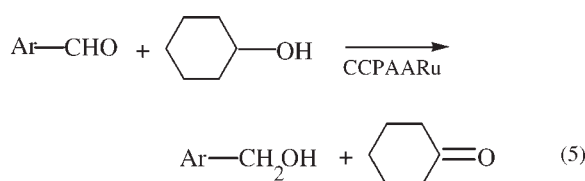
Table IV shows the transfer hydrogenation of 2,6-dichlorobenzaldehyde from cyclohexanol in the presence of CCPAARu (1.86 Ru%) catalysts at different alcohol concentrations. It was found that CCPAARu catalyst exhibited good activity for transfer hydrogenation of the aldehyde. The selectivity, metal leaching, recycling of CCPAARu catalyst, solvent effect and kinetic study of the systems will be reported in a subsequent publication.[39]

Transfer hydrogenation of aliphatic aldehyde by benzyl alcohol

We extend the CCPAARu catalysts for the transfer hydrogenation of aliphatic aldehydes reduced by benzyl alcohol. The catalyst, CCPAARu, here contains 2.91 Ru%. The transfer hydrogenation of the aliphatic aldehydes from benzyl alcohol could be described according to eq. (6).

$$R—CHO + \text{(benzene)}—CH_2OH \xrightarrow{CCPAARu} R—CH_2OH + \text{(benzene)}—CHO \quad (6)$$
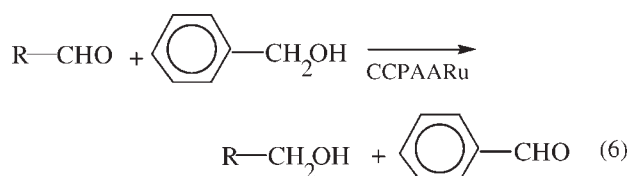
Table V shows the transfer hydrogenation of heptaldehyde from benzyl alcohol in the presence of the CCPAARu (2.91 Ru%) catalysts at different alcohol concentrations. It was found that CCPAARu catalyst exhibited good activity. The selectivity, metal leaching, recycling of CCPAARu catalyst, solvent effect and kinetic study of the systems will be reported in a subsequent publication.[40]

CONCLUSIONS

Complexes of ruthenium (II) with superabsorbent polyacrylates have been prepared starting with $RuH_2(PPh_3)_4$ in DMF reaction medium. The ruthenium content in the polymer was determined by DCP technique. It was shown that the ruthenium content in the polymer (1.5% AM) increased upon decreasing the initial —COO/Ru molar ratio, but ruthenium content decreased on increasing the crosslinking degree of polymer. IR spectra indicated that one mono-dentate and one bidentate species mainly coordinate to the metal center.

TABLE V
Transfer Hydrogenation of Heptaldehyde from Benzyl Alcohol in the Presence of
CCPAARu (2.91 Ru%) Catalysts (T = 140°C)

Ru × 10^3 (mmol)	Reaction medium	Alcohol (M)	Aldehyde (M)	Initial reaction rates (mM/min)	Conversion 24 h
8.64	Bromobenzene	0.08	0.17	0.17	78.4
8.64	Bromobenzene	0.13	0.17	0.27	88.6
8.64	Bromobenzene	0.17	0.17	0.43	90.6
8.64	Bromobenzene	0.35	0.17	0.46	90.9
8.64	Bromobenzene	0.52	0.17	0.50	95.8
8.64	Bromobenzene	0.69	0.17	0.52	95.8
8.64	Bromobenzene	0.86	0.17	0.53	96.9

Superabsorbent polyacrylate supported ruthenium (II) complexes as catalysts can be efficiently used for hydrogen transfer reduction of aldehydes. Sodium formate, cyclohexanol, and benzyl alcohol are used as hydrogen donors. Reaction media can be biphasic or organic phases.

References

1. Pittman, C. U., Jr. In Comprehensive Organometallic Chemistry; Wilkinson, G.; Stone, F. G. A.; Abel, G., Eds.; Pergamon: Oxford, 1982; Vol. 8, p 533.
2. Ciardelli, F.; Braca, G.; Carlini, C.; Sbrana, G.; Valentini, G. J Mol Catal 1982, 14, 1.
3. Tsuchida, E. Macromol Rev 1982, 16, 397.
4. Normura, K.; Kuromatsu, Y. J Mol Catal 2006, 245, 152.
5. Pittman, C. U., Jr. Polym News 2005, 30, 348.
6. Pittman, C.U., Jr.; Smith, L. R.; Hanes, R. M. J Am Chem Soc 1975, 97, 1742.
7. Grubbs, R. H.; Kroll, L. C. Polym Prepr Am Chem Soc Div Polym Chem 1971, 12, 423.
8. Grubbs, R. H.; Kroll, L. C. J Am Chem Soc 1971, 93, 3062.
9. Innorta, G.; Modelli, A.; Scagnolari, F.; Foffani, A. J Organomet Chem 1980, 185, 403.
10. Hines, L.; O'Driscoll, K. F.; Rempel, G. L. J Catal 1975, 38, 435.
11. Kabanov, V. A.; Smetanyuk, V. I. Makromol Chem Suppl 1981, 5, 121.
12. Braca, G.; Sbrana, G.; Carlini, C.; Ciardelli, F. In Catalysis: Heterogeneous and Homogeneous, Delmon, B.; Jannes, G., Eds.; Elsevier: Amsterdam, 1975; p 307.
13. Braca, G.; Carlini, C.; Ciardelli, F.; Sbrana, G. Sixth International Congress of Catalysis, London, A, Abstr. 43; 1976.
14. Valentini, G.; Cecchi, A.; Di Bungo, C.; Braca, G.; Sbrana, G. Homogeneous Heterogenous Catalysis; In Proceedings of Fifth International Symposium Related Homogeneous and Heterogenous Catalysis; 1986; p 765.
15. Liu, Z. S.; Rempel, G. L. J Appl Polym Sci 1997, 64, 1345.
16. Oga, S.; Abura, T.; Watanabe, Y. Organometallics 2002, 21, 2964.
17. Canivet, J.; Labat, G.; Stoeckli-Evans, H.; Süss-Fink, G. Eur J Inorg Chem 2005, 22, 4493.
18. Styles, P. MSc Thesis, University of Waterloo, Waterloo, Ontario, Canada; 1990.
19. Liu, Z. S.; Rempel, G. L. React Polym 1991, 14, 229.
20. Kott, L. University of Waterloo Report, Waterloo, Ontario, Canada; 1995.
21. Levinson, J. J.; Robinson, S. D. J Chem Soc A 1970, 2947.
22. Ito, T.; Kitazume, S.; Yamamoto, A.; Ikeda, S. J Am Chem Soc 1970, 92, 3011.
23. Braca, G.; Carlini, C.; Ciardelli, F.; Sbrana, G. In Proceedings VI International Congress Catalysis; Bond, G. C.; Wells P. B.; Tompkins, F. C., Eds.; Chem Soc London, 1977, 1, 528.
24. Chen, J.; Zhao, Y. J Appl Polym Sci 1999, 74, 119.
25. Lee, W. F.; Hsu, C. H. J Appl Polym Sci 1998, 69, 229.
26. Lee, W. F.; Hsu, C. H. J Appl Polym Sci 1997, 64, 1701.
27. Robinson, S. D.; Uttley, M. F. J Chem Soc Dalton Trans 1973, 18, 1912.
28. Sbrana, G.; Braca, G.; Giannetti, E. J Chem Soc Dalton Trans 1976, 18, 1847.
29. Bar, R.; Sasson, Y.; Blum, J. J Mol Catal 1984, 26, 324.
30. Bar, R.; Bar, L. K.; Sasson, Y.; Blum, J. J Mol Catal 33 1985, 33, 161.
31. Pinna, F.; Bonivento, M.; Strukul, G.; Graziani, E.; Cernia, E.; Palladino, N. J Mol Catal 1976, 1, 309.
32. Liu, Z. S.; Rempel, G. L. J Mol Catal A 2007, 278, 228.
33. Haddad, Y. M. Y.; Henbest, H. B.; Husbands, J.; Mitchell, T. B. R.; Trocha-Grimshaw, J. J Chem Soc Perkin Trans 1974, 1, 596.
34. Malunowicz, E.; Tyrlik, S. J Organomet Chem 1974, 72, 269.
35. Orr, J. C.; Mersereau, M.; Sanford, A. Chem Commun 1962, 162.
36. Sasson, Y.; Albin, P.; Blum, J. Tetrhadron Lett 1974, 14, 833.
37. Eliel, E. L.; Doyle, T. W.; Hutchins, R. O.; Gilbert, E. C. Org Synth 1970, 50, 13.
38. Imai, H.; Nishiguchi, T.; Fukuzumi, K. J Org Chem 1976, 41, 665.
39. Liu, Z. S.; Rempel, G. L. J Mol Cat, to appear.
40. Liu, Z. S.; Rempel, G. L. Applied Catalysis, to appear.